

PATENT SPECIFICATION

(11) 1 356 253

1 356 253

- (21) Application No. 21754/70 (22) Filed 6 May 1970
(21) Application Nos. 34428/70 and 34429/70
(22) Filed 16 July 1970
(23) Complete Specification filed 4 May 1971
(44) Complete Specification published 12 June 1974
(51) International Classification C09B 67/00, 35/08, 63/00
(52) Index at acceptance
C4P 2G2011 2H10 2H12 2H21 2H3 2H4 2H5 2H6 9A4B
9A5 F
C4A K
(72) Inventors GORDON FRANK BRADLEY and ROBERT BRUCE
McKAY

(19)



(54) AZO PIGMENT COMPOSITIONS

Best Available Copy

5

5

ERRATUM

10

SPECIFICATION No. 1,356,253

0

Page 1, line 33, *for* diazo *read* disazo

THE PATENT OFFICE

4th November, 1974

15

5

SPECIFICATION NO 1356253

Slip No 2

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of CIBA-GEIGY AG., a Swiss Body Corporate, of Basle, Switzerland.

THE PATENT OFFICE

R 78385/3

20

... which incorporated in printing inks. According to the invention, we prepare diarylide pigment compositions by coupling in water a tetrazotised pigment benzidine with a pigment coupling component, and we incorporate in the pigment whilst still in the water a water-soluble azo dyestuff; normally this will be a diazo diarylide dyestuff, but other classes of dyestuffs, such as monoazo dyestuffs or even dyestuffs such as diphenyl chrysoine, which as an example of a disazo (but not a diarylide) dyestuff can be used. In this specification, we use the terms pigment benzidine and pigment coupling component merely to differentiate the compounds forming the pigment from the compounds which are used to form the water-soluble azo dyestuff. The pigment benzidine and pigment coupling component used in the present invention are free from water-solubilising groups.

30

35

35

40

40

The incorporation of the water-soluble azo dyestuff may be carried out in a number of ways; in one process, we use a stoichiometric excess of the pigment coupling component over the tetrazotized pigment benzidine, and we add a minor proportion of

SEE ERRATA SLIP ATTACHED

SPECIFICATION AMENDED - SEE ATTACHED SLIP

PATENT SPECIFICATION

(11) 1 356 253

1 356 253

- (21) Application No. 21754/70 (22) Filed 6 May 1970
 (21) Application Nos. 34428/70 and 34429/70
 (22) Filed 16 July 1970
 (23) Complete Specification filed 4 May 1971
 (44) Complete Specification published 12 June 1974
 (51) International Classification C09B 67/00, 35/08, 63/00
 (52) Index at acceptance
 C4P 2G2011 2H10 2H12 2H21 2H3 2H4 2H5 2H6 9A4B
 9A5 F
 C4A K
 (72) Inventors GORDON FRANK BRADLEY and ROBERT BRUCE
 McKAY



(54) AZO PIGMENT COMPOSITIONS

(71) We, CIBA-GEIGY (U.K.) LIMITED, a British Company whose Registered Office address is 42 Berkeley Square, London, W.1. (Formerly known as Geigy (U.K.) Limited, a British Company, whose Registered Office address was Simonsway, Manchester 22), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pigment compositions, and is particularly concerned with the preparation of diarylide pigment compositions. Diarylide pigments are also known as benzidine pigments, but the former nomenclature is preferred according to modern usage.

The so-called benzidine yellow pigments are azo compounds, prepared by coupling tetrazotised 3:3'-dichlorobenzidine or a tetrazotised benzidine bearing further substituents in the aromatic nuclei with a coupling component which is an acetoacetaryl-amide. Normally 3:3'-dichlorobenzidine is used, but other substituted benzidines can be used; for example, pigments have been prepared from tetrachlorobenzidines. Examples of coupling components which have been used are acetoacetanilide, acetoacet-o-toluidide, acetoacet-p-toluidide, acetoacet-o-anisidide, acetoacet-o-chloranilide and acetoacet-2,4-xylylidide.

The so-called benzidine orange pigments are prepared in analogous manner by coupling tetrazotised 3:3'-dichlorobenzidine with a coupling component which is a 3-methyl-5-pyrazolone additionally substituted in the 1-position with a phenyl substituent which itself can bear up to five substituent groups such as alkyl, aryl, alkoxy or halogen groups.

Other diarylide pigments may be prepared by coupling tetrazotised derivatives of non-chlorinated benzidines with coupling components. One example of such a non-chlorinated benzidine which may be coupled to form a pigment is dianisidine, i.e. 3:3'-dimethoxy-benzidine.

We have now discovered how to prepare diarylide pigment compositions which have better colour strength and transparency properties than conventional diarylide pigments when incorporated in printing inks. According to the invention, we prepare diarylide pigment compositions by coupling in water a tetrazotised pigment benzidine with a pigment coupling component, and we incorporate in the pigment whilst still in the water a water-soluble azo dyestuff; normally this will be a diazo diarylide dyestuff, but other classes of dyestuffs, such as monoazo dyestuffs or even dyestuffs such as diphenyl chrysoine, which as an example of a disazo (but not a diarylide) dyestuff can be used. In this specification, we use the terms pigment benzidine and pigment coupling component merely to differentiate the compounds forming the pigment from the compounds which are used to form the water-soluble azo dyestuff. The pigment benzidine and pigment coupling component used in the present invention are free from water-solubilising groups.

The incorporation of the water-soluble azo dyestuff may be carried out in a number of ways; in one process, we use a stoichiometric excess of the pigment coupling component over the tetrazotised pigment benzidine, and we add a minor proportion of

SEE ERRATA SLIP ATTACHED

one or more tetrazotised sulphonated benzidines or tetrazotised carboxylated benzidines to the tetrazotised pigment benzidine before the coupling, or to a portion of the pigment coupling component before the coupling or to the reaction mixture during or after the coupling.

In another process, we may use a stoichiometric excess of the tetrazotised pigment benzidine over the pigment coupling component, and add a minor proportion of one or more coupling components containing water-solubilising functional groups to the pigment coupling component before the coupling, or to a portion of the tetrazotised pigment benzidine before the coupling or to the reaction mixture during or after the coupling.

The desired modification of the properties of diarylide pigments may also be achieved, according to the invention, by adding one or more water-soluble azo dyestuffs to the tetrazotised pigment benzidine before the coupling or to a portion of the pigment coupling component before the coupling or to the reaction mixture during or after the coupling, or to the previously prepared diarylide pigment, or by conducting the coupling of the pigment in a solution of such a water-soluble azo dyestuff. In such cases, the coupling component of the water-soluble azo dyestuff need not be the same as the coupling component in the pigment itself, nor need the respective tetrazotised benzidines be the same; indeed the water-soluble azo dyestuff need not in fact have a similar structure to that of the pigment it is being used to modify.

The water-soluble azo dyestuff may be prepared by coupling a water-solubilised tetrazotised benzidine with a coupling component not containing water-solubilising groups, or by coupling a tetrazotised benzidine with a coupling component containing water-solubilising groups, or by coupling a tetrazotised benzidine and a coupling component both of which contain water-solubilising groups. By water-solubilising groups we mean groups such as sulphonic acid and carboxylic acid groups and water-soluble metal salts thereof, amino groups and water-soluble salts of amino groups, for example those formed with aliphatic acids. The free acids of the water-soluble azo dyestuffs may be obtained, for example, by boiling solutions of the sodium salts of the water-soluble azo dyestuffs obtained in the coupling reactions in hydrochloric acid. Thus, for example, the pigment might be acetoacet-*o*-toluidide coupled to tetrazo-3:3'-dichlorobenzidine, and the water-soluble azo dyestuff could be acetoacetanilide coupled to tetrazo-4:4'-diamino-2:2'-biphenyl disulphonic acid; alternatively the pigment might be acetoacet-*m*-xylidide coupled to tetrazo-3:3'-dichlorobenzidine and the water-soluble azo dyestuff could be acetoacet-*m*-xylidide coupled to tetrazo-4:4'-diamino-2:2'-biphenyl disulphonic acid. Mixtures of water-soluble azo dyestuffs may be used.

The sulphonated or carboxylated benzidines used in the invention may be mono- or di-substituted, or may have more than two acid group substituents. Very suitable benzidines are disubstituted, that is they have one substituent sulphonic acid group or carboxylic acid group on each aromatic nucleus.

The exact mechanism by which the improvement in the benzidine pigment is obtained is not yet fully understood. It is however believed that some active species, most probably the water-soluble azo dyestuffs itself, is adsorbed onto the surface of the pigment particles, possibly affecting the growth of the particles and their crystalline nature, and modifying their final surface properties. The water-soluble disazo diarylide dyestuff may be rendered insoluble *in situ* in the composition. By this is meant that the water-soluble disazo diarylide dyestuff may be rendered insoluble at the adsorption stage. If desired, the adsorbed water-soluble azo dyestuff may be rendered insoluble at a later stage in the preparation of the pigment, for example by the formation of insoluble salts of metals of Groups IA, IB, IIA, IIB, IIIA, IIIB and VIII of the Periodic Table. One very suitable way of forming the water-insoluble salts is by a double decomposition reaction between the sodium salt of the water-soluble azo dyestuff and a water-soluble salt of the selected metal at an alkaline pH such as 8-9; typical soluble metal salts are zinc sulphate, magnesium sulphate, barium chloride, aluminium sulphate and calcium chloride. It may be desirable for the water-soluble azo dyestuff component in the pigment to be insolubilised in this way if there is a danger of the water-soluble azo dyestuff being washed off during the washing stage of the preparation of the treated pigment or of the water-soluble azo dyestuff bleeding into the fountain solution used in letterpress/lithographic printing processes. Furthermore, a hydrophilic surface on a pigment may cause bleeding into a fountain solution. The retention of the dye in the final pigment composition as a water-insoluble metal salt also gives the pigment further advantages.

The invention also includes the diarylide pigment compositions prepared in this way, and mixtures of two or more of such compositions. The compositions may be made

from a single pigment benzidine and different coupling components together with the water-soluble azo dyestuff, or from different pigment benzidines and a single coupling component together with the water-soluble azo dyestuff. In general the compositions will contain up to 25% by weight of water-soluble azo dyestuff calculated on the pigment; we prefer to incorporate from 1 to 10% by weight.

The water-soluble dyestuff may be prepared in situ. When this in situ preparation is employed the tetrazotised pigment benzidine is first reacted with one or more coupling components using the coupling component or components in an amount which constitutes a stoichiometric excess over the amount of tetrazotised pigment benzidine. The amount of coupling component or components which constitutes the excess over the above mentioned stoichiometric value is suitably such that there is in fact present the theoretical amount of coupling component or components required for complete stoichiometric coupling of the azo compound used in the in situ preparation of the water-soluble azo dyestuff or even a slight excess of coupling component or components over this theoretical amount say up to 5% by weight calculated on the other components to be coupled.

The sulphonated or carboxylated benzidines which may be used in the process according to the invention include the acids themselves, and their soluble metallic salts. The proportion of sulphonated or carboxylated benzidine may be up to 25% by weight of the pigment benzidine but we prefer to use not more than 10%. No further significant improvement is noted if larger proportions are used.

The additional incorporation into pigment compositions according to the invention of a resin or resinous material is found to enhance the flow properties of the compositions in letterpress varnishes. Examples of such resins or resinous materials are wood rosin and its derivatives such as hydrogenated wood rosin, and polyamide type resins such as are formed by condensation of phthalic anhydride and long chain amines. Furthermore the incorporation of surface-active agents, for example the naphthalene disulphonic acid/formaldehyde condensate sold under the Trade Mark "Belloid SF", is found to improve the tinctorial strength of the compositions in letterpress varnish, and the incorporation of nonionic surfactants such as long chain alcohols/ethylene oxide condensates and especially that one sold under the Trade Mark "Lubrol W", a cetyl alcohol ethylene oxide condensate, will improve gloss and texture in printing inks.

As has been stated, the pigment compositions produced according to our invention give products of high tinctorial strength, high gloss and good transparency when incorporated in letterpress ink varnish media. The texture and rheological properties of the compositions are not however completely satisfactory.

The solvent treatment of pigments is known. Such treatment in general results in pigments which are tinctorially weak, opaque in print and of low gloss, but which give good flowing inks when incorporated in letterpress ink varnish media. The texture of the pigment is again poor.

Furthermore it is known to treat azo pigments with fatty acids to obtain products with good colouring strength and pure brilliant tones; the products have the advantage that they are more easily filtered from finely dispersed suspensions for use in a dry state. No mention is made of the texture of the pigment.

Pigments which have good texture and which give letterpress inks of good strength, good transparency and good rheological properties are, in fact, very difficult to obtain. We have now surprisingly found that if we combine the preparation of pigment compositions according to our invention with a conventional solvent treatment, or with the addition of long chain fatty alcohol, diol or polyol, we obtain a pigment which not only has desirable qualities in letterpress inks, but which especially has good flow properties and transparency, facts which could not have been predicted from a knowledge of the effect of any of the processes alone. According to a further feature of the invention, therefore, we subject the pigment composition, in the aqueous state, to a conventional solvent treatment, or incorporate in it a fatty alcohol, diol, or polyol containing at least 8 and preferably 8 to 22 carbon atoms, which may or may not contain ether or ester linkages.

It is preferred that 0.1 to 30% by weight based on the weight of dry pigment of a fatty alcohol, diol or polyol containing from 8 to 22 carbon atoms is added to the pigment coupling component before the coupling, or to the pigment benzidine before or after diazotization and before the coupling, or to the reaction mixture during or after coupling.

It would be expected that two opposing mechanisms (dyestuff inhibiting crystallite

growth and solvent encouraging growth) would result in a compromise product, since flow properties can normally be related to transparency—the more opaque the better the flow. However, we find that we obtain the best out of both treatments with respect to transparency and flow.

Simple solvent treatment of pigments results in compositions possessing good flow properties (at low shear rates), and these produce opaque prints in inks. For multi-colour printing processes it is important that inks lay down as a transparent film. Hence to obtain both transparency of print and a good flowing ink is very important.

One specific example of a pigment whose properties can be dramatically improved in this way is that obtained from coupling acetoacet-*o*-anisidide and tetrazotised 3:3'-dichlorobenzidine, a benzidine yellow pigment. Compared with the pigment prepared in conventional manner, pigment in which a water-soluble coupled diarylide dyestuff is incorporated has improved rheological properties and almost equal tinctorial strength in letterpress ink media, and pigment which has been subjected to solvent treatment in the absence of dyestuff has improved rheological properties and lower tinctorial strength and gives more opaque prints in letterpress ink media. Pigment treated in both ways has improved rheological properties, almost maintains the tinctorial strength, gloss and transparency of untreated pigment, and shows improved texture.

The surface properties of azo pigment particles may be modified in a desirable manner if certain specific alcohols are present during the preparation of the pigment, or if the pigment is treated with these alcohols after it has been prepared by conventional methods. An azo pigment can be prepared by coupling a diazotised amino compound and a coupling agent, and adding a minor proportion of a fatty alcohol or diol or polyol containing from 8 to 22 and preferably at least 12 carbon atoms to the coupling agent before the coupling, or to the amino compound before or after diazotisation and before the coupling, or to the reaction mixture during the coupling, or to the pigment slurry resulting from the coupling. The pigment is then worked up in the usual way. A suitable process for the modification is disclosed in our copending Application No. 13677/70 (Serial No. 1299536) which described and claims a process in which an azo pigment is prepared by coupling a diazotised amino compound and a coupling agent, adding a minor proportion of a fatty alcohol, diol or polyol containing 12 or more carbon atoms to the coupling agent before the coupling, or to the amino compound before or after diazotisation and before the coupling, or to the reaction mixture during the coupling or to the pigment slurry resulting from the coupling, the amount of alcohol, diol or polyol being from 0.1 to 30% by weight of the weight of dry pigment itself being produced or being treated. Furthermore, it is also possible to obtain the modification of surface properties by the addition of the minor proportion of these alcohols, diols or polyols to a preformed azo pigment, for example by forming the pigment into an aqueous slurry, adding the alcohol, diol or polyol to the slurry with agitation and heating, and then filtering off and washing and drying the pigment.

If the alcohol, diol or polyol is to be added to one or other of the starting materials used in the preparation of the pigment, or is added to the reaction mixture in the course of the coupling, the timing of the various stages of the coupling and their temperature need not be significantly altered. When the alcohol, diol or polyol is added to a slurry of pigment, we have found that the time necessary to achieve the desired effect, that is to say before the pigment is filtered off, washed and dried, is not too critical and can range from a few minutes up to 2–3 hours. The production of azo pigments normally involves a step in which a slurry of the pigment is heated or boiled before the pigment is filtered off, and it is advantageous if the alcohol, diol or polyol is present at least during the heating step. This is not essential, however, and good results can be obtained at temperatures ranging from 0° C to 100° C.

The fatty alcohols to be used in the process according to the invention may be primary, secondary or tertiary alcohols, and may be saturated or unsaturated; the diols or polyols may contain primary, secondary or tertiary hydroxyl groups, and may also be saturated or unsaturated. Examples of suitable materials are cetyl alcohol, oleyl alcohol, behenyl alcohol, iso-octanol, 2-ethyl-hexan-1:3-diol. The amount of alcohol, polyol or diol may suitably be from 0.1 to 30% by weight of the weight of the dry pigment being produced or being treated, with amounts of from 0.1 to 10% by weight being preferred. When long chain alcohols, that is C_{16} – C_{22} , are used, analytical results show that more than 80% may be retained in the final pigment compositions; the proportion retained decreases as the chain length is reduced. This is predictable from a knowledge of the solubilities of fatty alcohols in water.

When the alcohol, diol or polyol is present during the coupling, or is added to the

reaction mixture during the coupling, it is advantageous if a non-ionic surface active agent such as the ethoxylated cetyl alcohol condensate sold under the Trade Mark "Lubrol W," is also present. It is found that oil inks prepared from pigment produced in this way have better flow properties and higher gloss than inks prepared from untreated pigment. It has also proved advantageous to add a metallic salt of a resin, or the free resin itself, to pigment which has been produced or treated according to the invention; it is found that inks prepared from the pigment then have better tinctorial strength and flow properties than do inks prepared from untreated pigment. Similarly it is found that the presence of resinous substances such as hydrogenated rosins also improves the printing performance of inks. Resins or resinous materials may be present from the start or may be added after the coupling stage of the process.

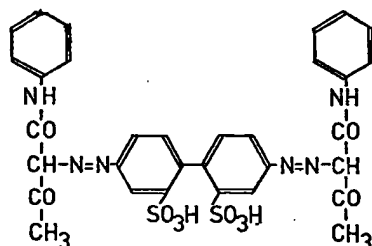
It has also been found that the presence of fatty acid such as oleic acid or stearic acid in the pigment composition improves the flow and the printing properties of inks. The acids may be added, preferably as their sodium salts, during or after the coupling stage or they may be present from the start. They may be rendered insoluble in the final pigment composition by conversion to sparingly soluble salts such as the calcium and zinc salts. The presence of fatty esters is similarly of value.

It is known that to treat diarylide pigments with up to 25% on pigment weight of high molecular weight fatty amines gives products showing excellent dispersibility in publication gravure ink media. Such products, however, show a defect in that the high colour strength initially developed is not maintained during storage of the ink.

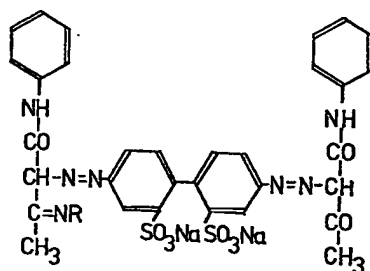
We have now surprisingly found that if we combine the preparation of pigment according to our invention with an amine treatment, we can prepare products having excellent dispersibility as well as having improved storage stability in ink media, a fact which could not have been predicted from a knowledge of the effect of either of the processes alone. According to a further feature of the invention, therefore, we incorporate in the pigment composition 0.1 to 35% calculated on the weight of pigment and dyestuff of an aliphatic amine, amine salt or amine oxide containing from 1 to 20 carbon atoms, and the products are then found to have excellent rheological properties in letter press inks.

The exact constitution of the pigment composition obtained by incorporating a water-soluble disazo diarylide dyestuff in a pigment and treating the composition with amine will depend on the water-soluble disazo diarylide dyestuff, on the ways in which the stages of the process are carried out, and on the proportion of amine or amine oxide used. Where a large amount of amine, say more than 10% is used, the products are stable to storage when used in gravure ink applications, whereas where up to 10% is used, the products show excellent transparency, strength, dispersibility and rheological properties in letterpress ink media. The amine or amine oxide may be present during the coupling or may be added to the tetrazotised pigment benzidine or to the pigment coupling component before the coupling, as well as being added in various ways to preformed pigment.

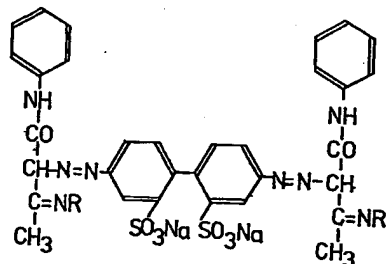
If a large quantity of an amine is used, and especially if the water-soluble azo dyestuff contains a reactive carbonyl group, then an azomethine dyestuff may be formed. For example, in the case of a pigment containing a sulphonated benzidine dyestuff of formula



an azomethine dyestuff may be formed, which may be envisaged as having the formula (in the presence of sodium ions)



the mono-azomethine, or



the diazomethine.

In these formulae, R is an alkyl group, containing from 1 to 20 carbon atoms, RNH_2 being the amine used in the process according to the invention. Depending on the pH, and the quantities and order of addition of the reactants, there may be water-soluble azo dyestuff, free amine, or amine salt or any combination of these present in the pigment, or there may also be present amine salt of the water-soluble azo dyestuff, azomethine of the water soluble azo dyestuff or amine salt of the azomethine of the water-soluble dyestuff.

If a tetrazotised pigment benzidine is coupled with a pigment coupling component, in the presence of a water-soluble azo dyestuff, an amine salt is added after the coupling, the pH raised to alkaline, say pH 10, and the slurry boiled, sodium or other alkali metal being the only metallic cation present, then it is found that the water-soluble azo dyestuff in the pigment product is in the form of its metal salt, no amine salt is present and no azomethine is present.

According to one embodiment of the present invention there is provided a process in which a salt of an amine containing 1 to 20 carbon atoms is added to an acidic aqueous slurry of the pigment composition, the pH is then raised to alkaline and the slurry is then boiled.

Alternatively, the slurry may first be boiled, then the amine salt added, and the pH subsequently raised, or the amine salt added to the slurry before the slurry is boiled, and the pH raised later. In each case it can be envisaged that during the coupling, the water-soluble azo dyestuff is adsorbing on to freshly precipitated particles and this stabilises the crystallite size of the pigment. No chemical reaction is occurring between the water-soluble azo dyestuff and the pigment. The amine salt is added and this also partly adsorbs on to the pigment particles and the excess amine is later flocculated on to the pigment's surface as free amine. Pigment formed in this way and dispersed into gravure ink media, is found to be stable to storage and to possess better tinctorial strength than a pigment which has merely been treated with amine in conventional manner. The pigment still retains the excellent dispersibility which is a feature of amine-treated pigments.

If the procedure first described is slightly altered, in that the pigment is coupled first in the presence of a water-soluble azo dyestuff, the slurry is made alkaline, say pH 10 again, the amine salt added to the alkaline slurry, and the slurry then boiled, analytical examination of the pigment shows that the metal content of the pigment has fallen below the theoretical amount required for the formation of metal dyestuff salt, and that free amine and amine salt of water-soluble azo dyestuff are present. Pigment formed in this way and dispersed into gravure ink media is found to be stable to storage and to possess better tinctorial strength than a pigment which has merely been treated with amine in conventional manner; the inks also have excellent rheolo-

gical properties, due, it may be asserted, to the presence of amine salt of water-soluble azo dyestuff.

Here again this procedure last described may be slightly modified with the same results; the slurry may be made alkaline and then boiled before the amine salt is added, or the slurry may be boiled, then made alkaline and the amine salt added. In each case the product is the same.

If the pigment is coupled in the presence of a water-soluble azo dyestuff, the slurry is kept acid, amine salt then added and the slurry boiled, amine salt itself is found to be present in the pigment product. The same result is obtained if the slurry is kept acid, boiled, and then the amine salt added.

A further way in which the process according to the invention may be carried out involves the incorporation of the water-soluble azo dyestuff into the pigment, the formation of a metal salt of the water-soluble azo dyestuff and then the addition of the amine. The adsorbed water-soluble azo dyestuff may be rendered insoluble by the formation of an insoluble salt of a metal of Groups IA, IB, IIA, IIB, IIIA, IIIB and VIII of the Periodic Table as hereinbefore described.

In these processes, the evidence suggests that an adsorbed layer of water-soluble azo dyestuff is built up during the pigment preparation. The addition of amine salts causes further adsorption on to the pigment surface as the amine group is attracted to acid groups of the water-soluble azo dyestuff. The combined effect of this doubly adsorbed layer is to protect the pigment particles during boiling and drying. It is believed that water-soluble azo dyestuff treatment itself controls the size of the primary pigment particles but does not give protection against cementation (aggregation) of the primary particles during the boiling and drying stages. The resulting pigment does not easily disperse in pigment carriers, that is it has bad texture. However, with amine treatment the particles are better protected against cementation during the boiling and drying processes, and products are produced with better texture; the rheological properties of the products in letterpress inks are improved greatly by this combined water-soluble azo dyestuff/amine treatment and are better than the properties of pigments which have been subjected to water-soluble azo dyestuff treatment alone, and than the properties of conventional pigments treated with amines.

The amines to be used in the invention may be primary, secondary or tertiary amines. Examples of amines are primary amines such as the product, mainly stearyl-amine sold under the Trade Mark "Armeen T," resin amines such as amine derivatives of wood rosin and allied compounds sold under the Trade Mark "Rosin Amine D," N-long chain alkylalkylene diamines such as those sold under the Trade Mark "Duomeen," polyamines such as N-cocotrimethylene diamine-N'-propylamine, polyamide/polyamine derivatives such as those sold under the Trade Mark "Merginamide," β -amines such as those sold under the Trade Marks "Armeen L11" and "Duomeen L15," ethoxylated fatty amines and diamines such as those sold under the Trade Marks "Ethomeen" and "Ethoduomeen," and derivatives of these compounds. Other specific amines are listed in the Examples later, for instance in Table 9 ("Casamine" and "Aromox" referred to in Table 9 are Registered Trade Marks).

As has been stated, processes according to the invention result in the production of pigments which may contain one or more of water-soluble azo dyestuff, free amine, amine salt, amine salt of water-soluble azo dyestuff and azomethine compound of water-soluble azo dyestuff, the formation of the last two mentioned of course depending on the existence of acid groups on the water-soluble azo dyestuff. Amine salts of water-soluble disazo diarylide dyestuff are novel compounds *per se*. When dispersed in gravure ink media the salts give desirable colouring properties with obvious advantages in tinctorial strength because of their partial solubility in the media.

Good results are also obtained, according to the invention, if the pigment composition is both subjected to a conventional solvent treatment, and has incorporated in it a minor proportion of an aliphatic amine, amine salt or amine oxide containing from 1 to 20 carbon atoms.

The invention will be exemplified with five classes of diarylide pigments, as follows:—

1. Benzidine Yellows:—

Name or Colour Index Number	Formed by coupling
Pigment Yellow 12 (Colour Index No. 21090)	3:3'-dichlorobenzidine and acetoacetanilide
Pigment Yellow 13 (Colour Index No. 21100)	3:3'-dichlorobenzidine and acetoacet-2,4-xylidide
Pigment Yellow 14 (Colour Index No. 21095)	3:3'-dichlorobenzidine and acetoacet- <i>o</i> -toluidide
Pigment Yellow 17 (Colour Index No. 21105)	3:3'-dichlorobenzidine and acetoacet- <i>o</i> -anisidide
Pigment Yellow 81	2:2':5:5'-tetrachlorobenzidine and acetoacet-2,4-xylidide
—	3:3'-dichlorobenzidine and acetoacet- <i>p</i> -toluidide
—	3:3'-dichlorobenzidine and acetoacet- <i>o</i> -chloranilidide

2. Benzidine Oranges:—

Name or Colour Index Number	Formed by coupling
Pigment Orange 13 (Colour Index No. 21110)	3:3'-dichlorobenzidine and 1-phenyl-3-methyl-5-pyrazolone
Pigment Orange 34 (Colour Index No. 21115)	3:3'-dichlorobenzidine and 1- <i>p</i> -tolyl-3-methyl-5-pyrazolone

3. Benzidine Reds:—

Name or Colour Index Number	Formed by coupling
Pigment Red 37 (Colour Index No. 21205)	3:3'-dimethoxybenzidine and 1- <i>p</i> -tolyl-3-methyl-5-pyrazolone
Pigment Red 41 (Colour Index No. 21200)	3:3'-dimethoxybenzidine and 1-phenyl-3-methyl-5-pyrazolone

4. Benzidine Blues:—

Name or Colour Index Number	Formed by coupling
Pigment Blue 25 (Colour Index No. 21180)	3:3'-dimethoxy-benzidine and anilide of 2-naphthol-3-carboxylic acid

5. Tolidine Yellows:—

Name or Colour Index Number	Formed by coupling
Pigment Yellow (Colour Index No. 21135)	3:3'-dimethylbenzidine and acetoacet-o-toluidide

Examples 1—67 illustrate specifically the treatment of pigment with water-soluble azo dyestuff, Examples 68—78 illustrate the treatment of pigment with water-soluble azo dyestuff and solvent, and Examples 79—129 illustrate the treatment of pigment with water-soluble azo dyestuff and amine or amine oxide.

Except where full details are given, the procedure used in Examples 1—67 is essentially as follows:—

A tetrazo solution is made in the usual way and kept at 0° C, and a coupling component is dissolved in caustic soda solution.

The tetrazotised benzidine is coupled to the coupling component by one of two procedures, usually at room temperature:—

(a) by reprecipitating the coupling component with dilute acid in a coupling vessel and running in the tetrazo solution over 1 hour, again usually at room temperature.

The pH of the coupling is normally 4 to 4.5

or

(b) the tetrazo solution and coupling component solution are run in together into a coupling vessel containing sodium acetate buffer. The pH again is controlled as in (a).

After coupling the slurry is raised to the boil and held at the boil for one hour. The slurry is then filtered, the pigment composition washed free of inorganic salts and dried at 50—55° C.

The water-soluble azo dyestuff can be added or made in situ at one of the four stages:—

1. Before the coupling stage
2. During the coupling stage
3. After the coupling stage
4. After the boiling stage

The addition of any metal salts is usually either at stages (3) or (4) to make the azo dyestuffs water-insoluble.

Example 1.

Solution (1): Tetrazo 3:3'-dichlorobenzidine was prepared by tetrazotising 26 parts of 3:3'-dichlorobenzidine in 500 parts of water at 0° C.

Suspension (2): Tetrazo 4:4'-diamino-2:2'-biphenyl disulphonic acid was prepared by tetrazotising 2.0 parts of 4,4'-diamino-2:2'-biphenyl disulphonic acid in 50 parts of water at 0° C.

Solution (3): 40.5 parts of acetoacetanilide were dissolved in a solution of 9.9 parts of sodium hydroxide in 900 parts of water.

A solution of 20 parts of sodium acetate in 200 parts of water was prepared in a coupling vessel. The pH was then adjusted to 4.5 with dilute acetic acid.

5% of solution (3) was added to the coupling vessel and then suspension (2) run in over the course of 10 minutes, ensuring that at no time was any substantial quantity of uncoupled tetrazo compound present. Solutions (1) and (3) were then run into the vessel simultaneously at ambient temperature, over the course of 1 hour, again no excess of tetrazo being allowed at any time, and the pH was controlled at 4.5 as necessary by addition of 10% sodium hydroxide solution. The reaction mixture was then raised to the boil, and boiled for 30 minutes, the pigment composition was filtered off, washed with water and dried at 50—55° C.

The pigment composition thus prepared when incorporated into a letterpress varnish had better colouring strength and greater transparency of print than had a pigment prepared simply by coupling 3:3'-dichlorobenzidine and acetoacetanilide.

Example 2.

The same solutions and reaction conditions were used as in Example 1, but the procedure was somewhat altered in that solution (1) and suspension (2) were first mixed together, and then coupled with solution (3). The pigment obtained was similar to that obtained in Example 1.

Example 3.

The same solutions and reaction conditions were used as in Example 1, but the procedure was somewhat altered in that solution (1) was first coupled with solution (3) and then suspension (2) was added to the reaction mixture. The pigment obtained was similar to that obtained in Example 1.

Example 4.

Solution (1) Tetrazo 3:3'-dichlorobenzidine was prepared by tetrazotising 26 parts of 3:3'-dichlorobenzidine in 500 parts of water at 0° C.

Suspension (2) Tetrazo 4:4'-diamino-2:2'-biphenyl disulphonic acid was prepared by tetrazotising 2.0 parts of 4,4'-diamino-2,2'-biphenyl disulphonic acid in 50 parts of water at 0° C.

Solution (3) 40.5 parts of acetoacetanilide was dissolved in a solution of 9.9 parts of sodium hydroxide in 900 parts of water.

A solution of 20 parts of sodium acetate in 200 parts of water was prepared in a coupling vessel. The pH was then adjusted to 4.5 with dilute acetic acid.

5% of solution (3) was added to the coupling vessel and then suspension (2) run in over the course of 10 minutes, ensuring that at no time was any substantial quantity of uncoupled tetrazo compound present. Solutions (1) and (3) were then run into the vessel simultaneously at ambient temperature, over the course of 1 hour, again no excess of tetrazo being allowed at any time, and the pH was controlled at 4.5 as necessary by addition of 10% sodium hydroxide solution. 2.4 parts of the resin based on abietic acid sold under the Trade Mark WW Rosin dissolved in 6.0 parts of 10% sodium hydroxide were added to the pigment slurry. The slurry was then boiled for 1 hour, the pH adjusted to 6-6.5 using 10% sodium hydroxide solution and 1.7 parts of zinc sulphate was added; the slurry was filtered and the pigment composition thus obtained washed with water, and dried at 50-55° C.

The pigment composition was similar to that obtained in Example 1, with the same advantages and better flow properties when incorporated into a letterpress varnish.

Example 5.

The procedure in Example 4 was repeated except that the WW Rosin was replaced by the hydrogenated abietic acid sold under the Trade Mark "Staybelite Resin". A pigment composition having similarly excellent properties was obtained.

Example 6.

The procedure of Example 4 was repeated twice except that in one case the WW Rosin was replaced by a resin prepared by the reaction of phthalic anhydride and dodecylamine, and in the other case by Beckacite 1624 (a rosin-modified cresylic acid). "Beckacite" is a Trade Mark. In each case, a pigment composition having similar excellent properties was obtained to that resulting from Example 4.

A range of water-soluble azo dyestuffs having the following general formula I and the respective substituents listed in the following Table I was incorporated into Pigment Yellow 12, Colour Index No. 21090, at each of the four possible stages of preparation outlined just before Example 1 above, added to the reaction mixture as an aqueous solution/slurry or prepared in situ.

The proportion of water-soluble azo dyestuff used in Examples 7 to 15 was 5% by weight based on the pigment dry weight.

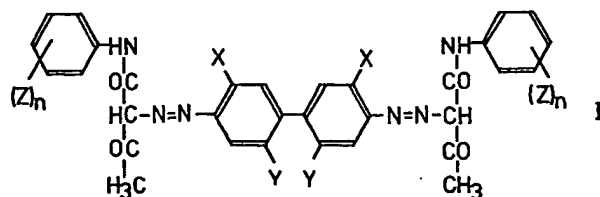


TABLE I

Example No.	X	Y	Z	n
7	Cl	H	4-SO ₃ Na	1
8	H	SO ₃ Na	4-SO ₃ Na	1
9	CH ₃	SO ₃ Na	H	1
10	CH ₃	SO ₃ Na	4-SO ₃ Na	1
11	H	CO ₂ Na	H	1
12	Cl	H	4-CO ₂ Na	1
13	H	SO ₃ (Ca) _{1/2}	H	1
14	H	SO ₃ (Ba) _{1/2}	H	1
15	Cl	H	p.NH ₂	1

Applicational advantages as previously described for the product prepared in Example 1 are found in each case.

Example 16.

Solution (1) Tetrazo 3:3'-dichlorobenzidine was prepared by tetrazotising 26 parts of 3:3'-dichlorobenzidine in 500 parts of water at 0° C.

Suspension (2) Tetrazo 4:4'-diamino-2:2'-biphenyl disulphonic acid was prepared by tetrazotising 2.0 parts of 4,4'-diamino-2:2'-biphenyl disulphonic acid in 50 parts of water at 0° C.

Solution (3) 46.9 parts of acetoacet-*m*-xylylide were dissolved in a solution of 9.9 parts of sodium hydroxide in 900 parts of water.

A solution of 20 parts of sodium acetate in 200 parts of water was prepared in a coupling vessel. The pH was then adjusted to 4.5 with dilute acetic acid.

5% of solution (3) was added to the coupling vessel and then suspension (2) run in over the course of 10 minutes, ensuring that at no time was any substantial quantity of uncoupled tetrazo compound present. Solutions (1) and (3) were then run into the vessel simultaneously at ambient temperature, over the course of 1 hour, again no excess of tetrazo being allowed at any time, and the pH was controlled at 4.5 as necessary by addition of 10% sodium hydroxide solution. The reaction mixture was then raised to the boil, and boiled for 30 minutes, the pigment composition was filtered off, washed with water and dried at 50—55° C.

The pigment composition thus prepared when incorporated into a letterpress varnish had better colouring strength and greater transparency of print than had a pigment prepared simply by coupling 3:3'-dichlorobenzidine and acetoacet-*m*-xylylide.

Example 17.

The same solutions and reaction conditions were used as in Example 16, but the procedure was somewhat altered in that solution (1) and suspension (2) were first mixed

together, and then coupled with solution (3). The pigment obtained was similar to that obtained in Example 16.

Example 18.

The same solutions and reaction conditions were used as in Example 16, but the procedure was somewhat altered in that solution (1) was first coupled with solution (3) and then suspension (2) was added to the reaction mixture. The pigment obtained was similar to that obtained in Example 16.

Example 19.

- (1) A tetrazo solution was made from 28.0 parts 3:3'-dichlorobenzidine in 500 parts water
(2) 46.85 parts of acetoacet-*m*-xylidide were dissolved in 900 parts water containing 9.15 parts of sodium hydroxide.

A solution of 20 parts of sodium acetate in 200 parts of water was prepared in a coupling vessel. The pH was then adjusted to 4.5 with dilute acetic acid. 5 parts of the sodium salt of the water-soluble azo dyestuff prepared from coupling tetrazo 4:4'-diamino-2:2'-biphenyl disulphonic acid and acetoacet-*m*-xylidide, dissolved in dilute sodium hydroxide solution, was added to the coupling vessel.

Solutions (1) and (2) were run into the vessel simultaneously at ambient temperature, over the course of 1 hour, no excess of tetrazo being allowed at any time, and the pH was controlled at 4.5 as necessary by addition of 10% sodium hydroxide solution. The reaction mixture was then raised to the boil, and boiled for 30 minutes, the pigment composition was filtered off, washed with water and dried at 50—55° C.

The pigment composition thus prepared had the same advantages over untreated pigment as are shown by the pigment composition of Example 16.

Example 20.

The procedure of Example 16 was repeated, up to the point where all the solutions had been coupled together. The pH was raised to 8—8.5 with dilute caustic soda solution, and 2 parts of barium chloride in 50 parts of water added. The reaction mixture was then boiled and filtered, and the pigment separated off was washed and dried as in Example 16.

The pigment obtained was similar to that resulting from the process of Example 16.

Example 21.

The procedure of Example 16 was again repeated, up to the point where all the solutions had been coupled together. The pH was then lowered to 1—2 with dilute hydrochloric acid, and the reaction mixture boiled and filtered; the pigment separated off was washed and dried as in Example 16.

The pigment obtained was similar to that obtained from the process of Example 16.

Examples 22, 23, 24.

The same solutions and reaction conditions were used as in Examples 16, 17 and 18 respectively except that 5:5'-dimethyl-4:4'-diamino-2:2'-biphenyl disulphonic acid (2 parts) replaced the 4:4'-diamino-2:2'-biphenyl disulphonic acid. The pigment compositions formed had advantages over untreated pigments, as in Example 16.

Examples 25, 26, 27.

The same solutions and reaction conditions were used as in Examples 16, 17, and 18 respectively except that 4:4'-diamino-3, 3'-biphenyl dicarboxylic acid (1.9 parts) replaced 4:4'-diamino-2:2'-biphenyl disulphonic acid. The pigment compositions formed had advantages over untreated pigments, as in Example 16.

Example 28.

The same solutions and reaction conditions were used as in Example 19 except that the water-soluble azo dyestuff prepared by coupling tetrazo 4:4'-diamino-2:2'-biphenyl disulphonic acid and acetoacetanilide replaced the water-soluble azo dyestuff prepared by coupling tetrazo 4:4'-diamino-2:2'-biphenyl disulphonic acid and acetoacet-*m*-xylidide. The pigment obtained was similar to that obtained in Example 16.

Example 29.

The same solutions and reaction conditions were used as in Example 19 except that the water-soluble dyestuff sold under the Trade Mark "Diphenyl Chrysoine 3 G," C.I. Direct Yellow 12, replaced the water-soluble azo dyestuff prepared from

coupling tetrazo 4:4'-diamino-2:2'-biphenyl disulphonic acid and acetoacet-*m*-xylidide. The pigment obtained was similar to that obtained in Example 16, with similar advantages.

Example 30.

5 The same solutions and reaction conditions were used as in Example 19 except that the water-soluble azo dyestuff prepared from coupling tetrazo 3:3'-dichlorobenzidine and acetoacetanilide-4-sulphonic acid (sodium salt) replaced the water-soluble azo dye used in Example 19. The pigment obtained had excellent properties.

Example 31.

10 The same solutions and reaction conditions were used as in Example 19 except that the water-soluble azo dyestuff prepared from coupling tetrazo 3:3'-dichlorobenzidine and acetoacetanilide-4-carboxylic acid replaced the water-soluble azo dye used in Example 19. The pigment obtained had excellent properties.

Example 32.

15 The same solutions and reaction conditions were used as in Example 19 except that the water-soluble azo dyestuff prepared from coupling tetrazo 3:3'-dichlorobenzidine and acetoacet-4-aminoanilide, as the acetate salt, replaced the water-soluble azo dye used in Example 19. A product similar to that resulting from Example 16 was obtained.

Example 33.

20 The procedure described in Example 16 was repeated. However, after boiling for 30 minutes, 1 part calcium chloride in 50 parts water was added. The pH was adjusted to 7.0 to 7.5 and the resulting pigment composition filtered off. The pigment composition obtained had similar excellent properties to the pigment composition obtained in Example 16.

Example 34.

30 The same solutions and reaction conditions were used as in Example 19 except that the water-soluble azo dyestuff prepared by coupling tetrazotised 4,4'-diamino-2,2'-biphenyl disulphonic acid to acetoacetanilide-4-sulphonic acid sodium salt replaced the water-soluble azo dyestuff prepared from coupling tetrazo 4,4'-diamino-diphenyl-2,2'-disulphonic acid and acetoacet-*m*-xylidide.

Examples 35, 36 and 37.

35 The same solutions and reaction conditions were used as in Examples 16, 17 and 18 respectively except that acetoacetorthotoluidide (43.7 parts) replaced the acetoacet-metaxylidide.

Enhanced colouring strength and transparency of print were found for these products over an untreated preparation of the same pigment.

Example 38.

40 Solution (1) Tetrazo 3:3'-dichlorobenzidine was prepared by tetrazotising 26 parts of 3:3'-dichlorobenzidine in 500 parts of water at 0° C.

Suspension (2) Tetrazo 4:4'-diamino-2:2'-biphenyl disulphonic acid was prepared by tetrazotising 2.0 parts of 4,4'-diamino-2:2'-biphenyl disulphonic acid in 50 parts of water at 0° C.

45 Solution (3) 2.5 parts of acetoacetanilide was dissolved in a solution of 0.6 parts of sodium hydroxide in 50 parts of water. This was added to a solution of 20 parts of sodium acetate in 200 parts of water in the coupling vessel. The pH was then adjusted to 6.5 with dilute acetic acid.

Suspension (2) was added to the coupling vessel over 10 minutes, ensuring that at no time was any substantial quantity of uncoupled tetrazo compound present.

50 Solution (4) 41.5 parts of acetoacetorthotoluidide was dissolved in 9.15 parts of sodium hydroxide in 900 parts of water. 5% of this solution was run into the coupling vessel. Solutions (1) and (4) were then run into the coupling vessel, over the course of 1 hour, again no excess of tetrazo being allowed at any time, and the pH was controlled at 4.5 as necessary by addition of 10% sodium hydroxide solution.

55 The reaction mixture was then raised to the boil, the pigment composition filtered off, washed with water and dried at 50—55° C.

Transparency, tinctorial strength and gloss improvements in letterpress varnishes over a non-treated pigment were found.

Example 39.

The procedure described in Example 38 was followed except that the water-soluble azo dyestuff prepared by coupling acetoacetanilide with aniline 2,5 disulphonic acid was used. The pigment composition obtained had similar advantages over non-treated pigment to the pigment composition of Example 38.

Examples 40 to 48.

A range of water-soluble azo dyestuffs having the general formula I and the specific substituents listed in the following Table 2 was incorporated into Pigment Yellow 14, Colour Index No. 21095, at each of the four possible stages of preparation outlined just before Example 1, added to the reaction mixture as an aqueous slurry/solution or prepared in situ.

The proportion of water-soluble dyestuff used in Examples 40 to 43 was 5% based on the weight of pigment.

TABLE 2

Example No.	X	Y	Z	n
40	Cl	H	4-SO ₃ Na	1
41	H	SO ₃ Na	4-SO ₃ Na	1
42	CH ₃	SO ₃ Na	H	1
43	CH ₃	SO ₃ Na	2-CH ₃	1

Applicational advantages as previously described are found in each case.

The general procedures described were repeated with the benzidine yellow pigments and the dyestuffs set out in the following Table 3. The water-soluble azo dyestuffs again had the formula I previously defined and were used in the proportion of 5% by weight based on the weight of the pigment.

TABLE 3

Example No.	Pigment	X	Y	Z	n
44	Pigment Yellow 17	H	SO ₃ Na	2-OCH ₃	1
45	Pigment Yellow 81	Cl	Cl	4-SO ₃ Na	1
46	3,3'-Dichlorobenzidine coupled with acetoacet- <i>p</i> -toluidide	H	SO ₃ Na	<i>p</i> -CH ₃	1
47	3,3'-Dichlorobenzidine coupled with acetoacet- <i>o</i> -chloranilide	H	SO ₃ Na	<i>o</i> -Cl	1
48		CH ₃	SO ₃ Na	<i>o</i> -Cl	1

Applicational advantages as previously described are found in each case.

Example 49.

A tetrazo solution was prepared from 50.6 parts 100% 3:3'-dichlorobenzidine as the hydrochloride in 1500 parts of water at 0° C.

A suspension of 72 parts of 1-phenyl-3-methyl-5-pyrazolone in 1500 parts water was buffered with 50 parts of sodium acetate.

The tetrazo solution was run into the pyrazolone suspension over one hour. The pH of the solution was controlled at 4.0—4.5. After coupling the slurry was split into 5 parts.

Part A The slurry was filtered, the pigment obtained washed with water and dried at 50° C.

Part B The slurry was boiled for one hour, filtered, the pigment obtained washed with water and dried at 50° C.

5 *Part C* To the slurry was added 5% by pigment weight of a water-soluble azo dyestuff prepared from coupling tetrazo benzidine-2:2'-disulphonic acid and 1-(*p*-sulpho-phenyl)-3-methyl-5-pyrazolone.

The resulting slurry was boiled for one hour, filtered and the pigment composition washed with water and dried at 50—55° C.

10 *Part D* The slurry was heated to 90° C, and held at 90° C for 10 minutes, 5% of the same dyestuff added as was added to part C and the slurry boiled for 30 minutes. The slurry was then filtered, the pigment composition washed with water, and dried at 50—55° C.

15 *Part E* The slurry was boiled for 30 minutes, 5% of the same dyestuff added, the slurry was filtered, and the pigment composition washed free of salt and dried at 50—55° C.

20 In letterpress varnishes the pigment composition resulting from *A* was identical to that resulting from *C* in hue, transparency and gloss, *B* was identical to *E*, both *B* and *E* being lower in transparency and gloss than *A* and *C*, and *D* had properties in between *A* and *B*. This illustrates the stabilisation of the pigment by the water-soluble azo dyestuff at the stage the dyestuff is added.

Examples 50 to 54.

25 A range of water-soluble azo dyestuffs of the following general formulae II and III and having the actual substituents specified in the following Table 4 was incorporated into Pigment Orange 15, Colour Index No. 21130, at each of the four possible stages of preparation outlined just before Example 1, added to the reaction mixture as an aqueous solution/slurry or prepared in situ.

The proportion of water-soluble azo dyestuff used in Examples 50 to 54 was 5% by weight based on the pigment dry weight.

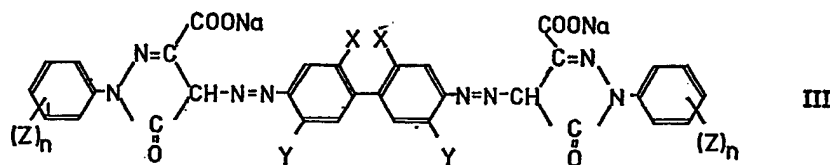
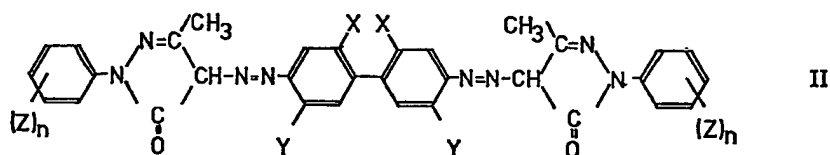


TABLE 4

Example	Dyestuff Formula	X	Y	Z	n
50	II	H	SO ₃ Na	H	1
51		Cl	H	4-SO ₃ Na	1
52		H	SO ₃ Ca $\frac{1}{2}$	H	1
53	III	H	H	H	1
54		H	H	3-NH ₂	1

Applicational advantages as previously described are found in each case.

Example 55.

Solution (1) Tetrazo 3,3'-dichlorobenzidine was prepared by tetrazotising 77.1 parts of 3,3'-dichlorobenzidine in 1500 parts of water at 0° C.

Suspension (2) Tetrazo 4,4'-diamino-2,2'-biphenyl disulphonic acid was prepared by tetrazotising 5.35 parts 4,4'-diamino-2,2'-biphenyl disulphonic acid in 100 parts water at 0° C.

Solution (1) and Suspension (2) were mixed to give suspension (4).

Solution (3) 126 parts of 1-p-tolyl-3-methyl-5-pyrazolone were dissolved in a solution of 37.8 parts sodium hydroxide in 900 parts of water.

A solution of 7.2 parts sodium acetate in 2000 parts water was then prepared in a coupling vessel. The pH was adjusted to 5.0 with dilute hydrochloric acid and solution (3) and suspension (4) run in simultaneously at ambient temperatures over the course of 30 minutes ensuring that at no time was any substantial quantity of uncoupled tetrazo present.

The resultant slurry was then heated to 90° C and held for 30 minutes. The pigment composition was filtered off, washed with water and dried at 50—55° C.

The pigment composition thus prepared had a superior colouring strength, gloss and transparency when incorporated into letterpress varnish to the pigment prepared simply by coupling 3,3'-dichlorobenzidine and 1-p-tolyl-3-methyl-5-pyrazolone.

Example 56.

Solution (1) Tetrazo 3,3'-dichlorobenzidine was prepared by tetrazotising 50.6 parts of 3,3'-dichlorobenzidine in 1000 parts of water at 0° C.

Solution (2) 77.0 parts of 1-p-tolyl-3-methyl-5-pyrazolone were dissolved in a solution of 23.0 parts sodium hydroxide in 500 parts of water.

A solution of 5.5 parts of sodium acetate in 1500 parts of water was then prepared in a coupling vessel I. Solutions (1) and (2) were run in simultaneously at ambient temperature over the course of 30 minutes ensuring that no time was any substantial quantity of uncoupled tetrazo present. This gave slurry I.

Solution (3) Tetrazo 3,3'-dichlorobenzidine was prepared by tetrazotising 2.1 parts of 3,3'-dichlorobenzidine in 50 parts of water at 0° C.

Solution (4) 4.4 parts of 1-p-sulphophenyl-3-methyl-5-pyrazolone were dissolved in a solution of 1.5 parts of sodium hydroxide in 50 parts of water.

A solution of 2.0 parts of sodium acetate in 200 parts of water was then prepared in a coupling vessel II. Solutions (3) and (4) were run in simultaneously at ambient temperature over the course of 10 minutes ensuring that at no time was any substantial quantity of uncoupled tetrazo present. This gave slurry II.

Slurry II was then added to slurry I and the mixture was heated to 90° C, filtered, washed with water and dried at 50° C.

The advantages of this pigment composition over non-treated pigment prepared simply by coupling 3:3'-dichlorobenzidine and 1-p-tolyl-3-methyl-5-pyrazolone are similar to those of the pigment composition prepared in Example 55.

Example 57.

Solution (1) Tetrazo 3,3'-dichlorobenzidine was prepared by tetrazotising 77.1 parts of 3,3'-dichlorobenzidine in 1500 parts of water at 0° C.

Suspension (2) Tetrazo 4,4'-diamino-2,2'-biphenyl disulphonic acid was prepared by tetrazotising 5.35 parts, 4,4'-diamino-2,2'-biphenyl disulphonic acid in water at 0° C.

Solution (3) 126 parts 1-*p*-tolyl-3-methyl-5-pyrazolone were dissolved in a solution of 37.8 parts sodium hydroxide in 900 parts of water.

A solution of 7.2 parts sodium acetate in 2000 parts water was then prepared in a coupling vessel. The pH was adjusted to 5.0 with dilute hydrochloric acid and solutions (1) and (3) run in simultaneously at ambient temperature over the course of 30 minutes ensuring that at no time was any substantial quantity of uncoupled tetrazo present.

Suspension (2) was then added over 10 minutes to the reaction mixture from solutions (1) and (3) and the resultant reaction mixture heated to 90° C. for 30 minutes. The pigment was filtered off, washed with water and dried at 50—55° C.

The pigment thus prepared had a superior colouring strength when incorporated into letterpress varnish to the pigment prepared simply by coupling 3,3'-dichlorobenzidine and 1-*p*-tolyl-3-methyl-5-pyrazolone.

Example 58.

Suspension (1) Tetrazo 4,4'-diamino-2,2'-biphenyl disulphonic acid was prepared by tetrazotising 2.6 parts of 4,4'-diamino-2,2'-biphenyl disulphonic acid at 0° C.

Solution (2) 3.9 parts of 1-*p*-sulphophenyl-3-methyl-5-pyrazolone were dissolved in a solution of 1.4 parts of sodium hydroxide in 50 parts of water.

Solution (3) Tetrazo 3,3'-dichlorobenzidine was prepared by tetrazotising 50.6 parts of 3,3'-dichlorobenzidine in 1000 parts of water at 0° C.

Solution (4) 77.0 parts of 1-*p*-tolyl-3-methyl-5-pyrazolone were dissolved in a solution of 23.0 parts sodium hydroxide in 500 parts of water.

A solution of 5.5 parts of sodium acetate in 1500 parts of water was then prepared in a coupling vessel.

Suspension (1) and Solution (2) were then run in simultaneously at ambient temperature over the course of 10 minutes ensuring that at no time was any substantial quantity of uncoupled tetrazo present.

After this, solutions (3) and (4) were then run in simultaneously at ambient temperature over the course of 30 minutes ensuring that at no time was any substantial quantity of uncoupled tetrazo present.

The resultant slurry was then heated to 90° C held at 90° C for 30 minutes, filtered and the pigment composition washed with water and finally dried at 50° C.

Advantages of this pigment composition are similar to those of the composition of Example 55.

Example 59.

Solution (1) Tetrazo 3,3'-dichlorobenzidine was prepared by tetrazotising 77.1 parts of 3,3'-dichlorobenzidine in 1500 parts of water at 0° C.

Suspension (2) Tetrazo 4,4'-diamino 2,2'-biphenyl disulphonic acid was prepared by tetrazotising 5.35 parts 4,4'-diamino-2,2'-biphenyl disulphonic acid in water at 0° C.

Solution (3) 6.2 parts of acetoacetanilide was dissolved in a solution of 2 parts of sodium hydroxide in 50 parts of water. This was added to a solution of 7.2 parts sodium acetate in 2000 parts water in a coupling vessel. Suspension (2) was run into the coupling vessel over 10 minutes, ensuring that no excess of tetrazo was present.

Solution (4) 120 parts of 1-*p*-tolyl-3-methyl-5-pyrazolone were dissolved in a solution of 36.0 parts sodium hydroxide in 900 parts of water. 5% of this solution was added to the coupling vessel.

Solutions (1) and (4) were run in simultaneously into a coupling vessel over the course of 30 minutes ensuring no excess of tetrazo was present. The pH of coupling was maintained at 4.5 by adding the required amount of 10% sodium hydroxide during the coupling process.

The slurry was heated to 90° C, filtered and the pigment composition washed with water and dried at 50—55° C.

The pigment composition thus prepared had a superior colouring strength when

incorporated into letterpress varnish to the pigment prepared simply by coupling 3,3'-dichlorobenzidine and 1-p-tolyl-3-methyl-5-pyrazolone.

Example 60.

The conditions for this preparation are identical to those of Example 58 except that 5% of the formaldehyde condensate with naphthalene disulphonic acid sold under the Trade Mark "Belloid SFD" is added before the coupling stages to the coupling vessel.

The pigment composition is found to have greater tinctorial strength than that of Example 58 when incorporated in letterpress varnish.

Examples 61 to 64.

Further water-soluble azo dyestuffs were incorporated in Pigment Orange 34 as in the following Table 5, at each of the possible stages of preparation outlined above, added to the reaction mixture as an aqueous solution/slurry or prepared in situ. The water-soluble azo dyestuffs had the formula II as previously defined and were used in the proportion of 5% by weight based on the pigment dry weight.

TABLE 5

Example	X	Y	Z	n
61	H	SO ₃ Na	H	1
62	H	SO ₃ Ba $\frac{1}{2}$	H	1
63	H	SO ₃ Na	4-SO ₃ Na	2
64	Cl	H	4-SO ₃ Na	2

Applicational advantages as previously described are found in each case.

Examples 65 and 66.

Two benzidine reds were treated with water-soluble azo dyestuff of formula II above, as in the following Table 6. The proportion of water-soluble azo dyestuff used was 5% by weight based on the pigment dry weight.

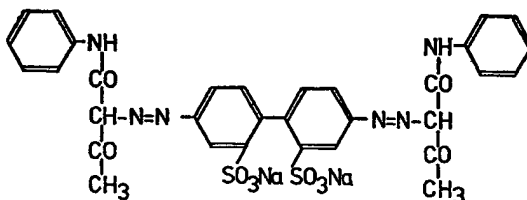
TABLE 6

Example	Pigment	X	Y	Z	n
65	Pigment Red 37	H	SO ₃ Na	4-SO ₃ Na	1
66	Pigment Red 41	H	SO ₃ Na	4-SO ₃ Na	1

Pigment composition prepared according to these two examples show excellent transparency in letterpress varnish.

Example 67.

The yellow pigment, Colour Index No. 21135 was treated at each of the four stages of preparation listed above with the water-soluble azo dyestuff having the formula



The proportion of the water-soluble azo dyestuff used was 5% by weight based on the pigment dry weight.

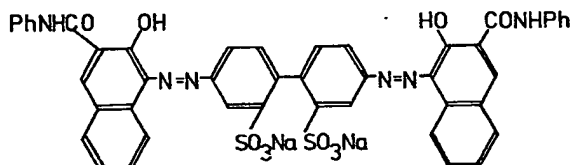
Applicational advantages as previously described are found in each case.

Example 68.

5 Solution (1): Tetrazo 3,3'-dimethoxy-benzidine was prepared by diazotising 30.5 parts of 100% 3,3'-dimethoxy-benzidine with hydrochloride acid and 18.2 parts of sodium nitrite giving a final volume of 550 parts at a temperature of 0° C.

10 Solution (2): A solution of 36 parts of sodium hydroxide and 8 parts of Turkey Red Oil in 800 parts of water was heated to 70° C. 69.7 parts of Naphthol AS (2-hydroxynaphthalene-3-carboxanilide) were added slowly with stirring giving a final volume of 1200 parts and a temperature of 25° C.

Solution (3): 5 parts of the water-soluble azo dyestuff having the formula:—



15 prepared by coupling tetrazo benzidine-2,2'-disulphonic acid with Naphthol AS were dissolved in a 10% solution of sodium hydroxide.

20 Solution (1) was run into solution (2), the pH being maintained above 10.5 by suitable addition of 10% sodium hydroxide solution. When the coupling was complete, the pH of the suspension was lowered to 5.0 and solution (3) was added. The slurry was then boiled for 1 hour and the product filtered off, washed and dried at 50—55° C.

The pigment composition had superior gloss and tinctorial strength in letterpress varnish or the product of a similar process in which the water-soluble azo dyestuff was omitted.

25 Examples 69 to 79 illustrate the further modification of pigment/dyestuff compositions according to the invention by treatment with a solvent, or by addition of a fatty acid or fatty acid ester, fatty alcohol, diol or polyol. These can be added to the reaction mixture at any of the four stages of preparation of the pigment composition at which the water-soluble azo dyestuff can be added.

Example 69

30 The pigment compositions described in Examples 1, 2 and 3 were treated with 5%, based on the weight of pigment, of solvent or fatty alcohol, diol or polyol after the coupling stage but before boiling. The following materials were used:—

35 Cetyl alcohol, oleyl alcohol, iso-octanol, 2-ethylhexan-1,2-diol, polyethylene glycol 600, xylene, dibenzyl ether, dipropylene glycol monolaurate, *o*-dichlorobenzene, nitrobenzene, benzyl cyanide and quinoline.

40 The resulting compositions were tested in comparison with untreated Pigment Yellow 12, solvent treated Pigment Yellow 12, and with the compositions prepared strictly according to Examples 1, 2 and 3; in each case there was improved flow and texture over pigment merely treated with water-soluble azo dyestuff, and superior strength and transparency to untreated pigment, or to pigment treated with solvent alone.

Example 70.

45 (1) A tetrazo solution was made from 26.00 parts 3:3'-dichloro-benzidine in 500 parts water.

(2) A tetrazo suspension was made from 2.000 parts 4:4'-diamino-2:2'-biphenyl di-sulphonic acid in 120 parts water.

50 46.85 parts of acetoacet-*meta*-xylylidide were dissolved in 900 parts water containing 9.15 parts of sodium hydroxide. The acetoacet-*m*-xylylidide was then precipitated by adding a solution of 13.75 parts of glacial acetic acid in 50 parts of water, with the formation of a slurry.

Tetrazo solution (1) was then added over 1½ hours to the slurry of precipitated acetoacet-*m*-xylylidide. The pH of the reaction mixture was maintained between 4.0

and 4.5 during the addition by the simultaneous addition of a 10% aqueous solution of sodium hydroxide.

The pH of the yellow pigment slurry obtained was then adjusted to pH 6.0 with 10% sodium hydroxide. Tetrazo suspension (2) was then added over 15 minutes to the slurry. The pH of the slurry was maintained between 5.5 and 6.0 during the addition by the simultaneous addition of a 10% aqueous solution of sodium hydroxide.

4 parts of dibenzyl ether were then added to the pigment slurry. The slurry was boiled for 1 hour and the pH was adjusted with 10% caustic soda solution to 8.0—9.0. The pigment was then isolated by filtering, washing the filter cake free of water-soluble impurities, and drying at 50° C.

The pigment composition obtained by this process, when incorporated into a letter-press varnish ink medium, gave more glossy and transparent prints and greater tinctorial strength than did a pigment composition treated with solvent only (no dyestuff treatment). Rheological properties of the ink were similar to those of an ink prepared from pigment treated with solvent only.

Example 71.

The procedure described in Example 70 was repeated, except that 4 parts of *o*-dichlorobenzene were used instead of 4 parts of dibenzyl ether. The pigment composition resulting had similar properties to the pigment obtained in Example 69.

Example 72.

(a) The procedure described in Example 16 was followed except that an addition of 5% based on the pigment weight of cetyl alcohol was made before the pigment suspension was boiled and filtered.

(b) The procedure described in Example 16 was followed except that an addition of 5% based on the pigment weight of oleic acid was made before the pigment suspension was boiled and filtered.

In each case the product had superior flow and texture to that of the product of Example 16 while largely retaining the desirable high transparency. In both cases similar results could be obtained by making the addition before or during the coupling.

Example 73.

The procedure described in Example 35 was followed except that an addition of 5% based on the pigment weight of:—

- (a) cetyl alcohol
- (b) tetralin
- or (c) polyethylene glycol 600

was made before the pigment suspension was boiled and filtered. In each case the product had superior flow properties to those of the pigment obtained in Example 35 while the strength and transparency advantages of that pigment composition were largely maintained.

Similar results were obtained by making the additions before or during the coupling.

Example 74.

(1) A tetrazo solution was made from 27.4 parts of 3:3'-dichlorobenzidine in 500 parts water.

(2) A tetrazo suspension was made from 1.5 parts 4:4'-diamino-2:2'-biphenyl disulphonic acid in 100 parts water.

49 parts of acetoacet-*o*-anisidide were dissolved in a solution of 9.2 parts of sodium hydroxide/900 parts of water. The coupling component was then precipitated by the addition of 14 parts of glacial acetic acid in 50 parts of water, with the formation of a slurry.

Tetrazo solution (1) was then added over 1 hour to the slurry. The pH of the reaction mixture was maintained between 4.0 and 4.5 during the addition by simultaneous addition of a 10% aqueous solution of sodium hydroxide.

The pH of the yellow pigment slurry obtained was then adjusted to pH 6.0—7.0 with 10% sodium hydroxide solution. Tetrazo suspension (2) was then added over 15 minutes to the slurry. The pH of the slurry was maintained between 6.0—7.0 during the addition by the simultaneous addition of a 10% aqueous solution of sodium hydroxide.

A suspension of 4 parts of cetyl alcohol in 25 parts water was added and the

slurry was boiled for 1 hour. The slurry was then filtered, washed salt-free and dried at 50—55° C.

The resulting pigment composition when incorporated into a letterpress printing ink varnish medium gave improved rheological properties over a pigment composition obtained by simply coupling acetoacet-*o*-anisidide with tetrazo 3:3'-dichlorobenzidine. No significant loss of tinctorial strength was found over untreated pigment.

Example 75.

The procedure described in Example 74 was followed except that 5% based on the pigment weight of

- (a) tetralin
or (b) oleic acid

was added before the pigment suspension was boiled and filtered off. The resulting pigments exhibited excellent flow and transparency.

Similar results are obtained when the additions are made at an earlier stage of preparation.

Example 76.

The procedure described in Example 47 was carried out except that 5% based on the pigment weight of

- (a) cetyl alcohol
(b) tetralin
or (c) polyethylene glycol 600

were incorporated before the pigment suspension was boiled and filtered. Again the products from these treatments had enhanced flow properties and transparency.

Example 77.

The procedure described in Example 49 Part C was followed with the exception that 5% based on the pigment weight of tetralin was added before the pigment suspension was boiled. The resulting pigment composition had excellent flow properties and transparency.

Example 78.

Solution (1) — Tetrazo 3,3'-dichlorobenzidine was prepared by tetrazotising 77.10 parts 3,3'-dichlorobenzidine in 1500 parts water at 0° C.

Suspension (2) — Tetrazo 4,4'-diamino-2,2'-biphenyl disulphonic acid was prepared by tetrazotising 5.35 parts 4,4'-diamino-2,2'-biphenyl disulphonic acid in water at 0° C.

Solution (3) — 126 parts 1-*p*-tolyl-3-methyl-5-pyrazolone were dissolved in a solution of 37.8 parts sodium hydroxide in 900 parts water.

A solution of 7.2 parts sodium acetate in 2000 parts water was then prepared in a coupling vessel. The pH was adjusted to 5.0 with dilute hydrochloric acid and solutions (1) and (3) run in simultaneously at ambient temperature over the course of 30 minutes ensuring that at no time was any substantial quantity of uncoupled tetrazo present. Suspension (2) was then added over 10 minutes to the reaction mixture from solutions (1) and (3).

5 parts of cetyl alcohol suspended in 50 parts of water was then added to the reaction mixture. The resultant reaction mixture was heated to 90° C and held at 90° C for 30 minutes. The pigment was filtered off, washed with water and dried at 50—55° C. When incorporated into a letterpress varnish, the pigment thus prepared had a colouring strength up to 15% greater than the pigment prepared simply by coupling 3,3'-dichlorobenzidine and 1-*p*-tolyl-3-methyl-5-pyrazolone. The rheological properties of the letterpress ink are much better than those of a similar ink prepared with an untreated pigment.

Example 79.

The procedure described in Example 78 was repeated except that 5% based on the pigment weight of tetralin replaced the cetyl alcohol there used.

The properties of the pigment resulting from this treatment were similar to those of the pigment obtained from Example 78.

Examples 80 to 130 illustrate the treatment of pigment compositions according to the invention with amine or amine oxide. The amine or amine oxide can be added to the reaction mixture at any of the four stages of preparation of the pigment composition

at which the water-soluble azo dyestuff can be added. The Examples are split into two groups, Nos. 80—100 and Nos. 101—130; the first group shows the addition of more than 10% of amine or amine oxide for gravure ink applications; the second group shows the addition of less than 10% amine or amine oxide for letterpress and lithographic ink application.

Example 80.

Solution (1) 67 parts of acetoacetanilide were dissolved in a solution of 28.2 parts of sodium hydroxide in 900 parts of water.

Solution (2) 43.5 parts of 3:3'-dichlorobenzidine were tetrazotised in the usual manner with 24.1 parts of sodium nitrite in 800 parts of water at 0° C.

Suspension (3) 4.1 parts of 5:5'-dimethyl-4:4'-diamino-2:2'-biphenyl disulphonic acid were tetrazotised in the usual manner with 1.7 parts of sodium nitrite in 125 parts of water at 0° C.

10% of solution (1) was run into a coupling vessel and suspension (3) was then added over the course of 10 minutes, ensuring that at no time was any substantial quantity of uncoupled tetrazo compound present.

The remainder of solution (1) and solution (2) were then added simultaneously to the reaction mixture over the course of 1 hour. The reaction temperature was maintained at or about ambient temperature, and the pH between 4.5 and 4.8, again no substantial quantity of uncoupled tetrazo compound being present at any time.

28.2 parts of the amine mixture sold under the Trade Mark "Armeen T" (believed to consist essentially of palmityl, stearyl and oleyl amines) were dissolved in 17.0 parts of glacial acetic acid in 1000 parts of water and added to the coupling vessel. The reaction mixture was then raised to the boil, and boiled for 30 minutes; the pH of the reaction mixture slurry after this boiling was adjusted to 10.0 with sodium hydroxide solution at 70° C. The pigment composition was then filtered off, washed with water and dried at 50—55° C.

The pigment composition obtained in this way was readily dispersible in roto-gravure ink media, giving a storage-stable ink, and was tinctorially stronger and more transparent, resulting also in a glossier product, than the benzidine yellow pigment composition obtained simply by coupling 3:3'-dichlorobenzidine and acetoacetanilide in the presence of Armeen T. A pigment composition produced without using Armeen T or similar amine or combination of amine is not readily dispersible in roto-gravure ink media.

Example 81.

Solutions (1) and (2) and suspension (3) were prepared as in Example 80 and a solution of Armeen T as in Example 80 was also prepared. All of solution (1) was added to the coupling vessel and the pH was adjusted to below 7.0 with dilute acid and then solution (2) and suspension (3) were mixed and added to the vessel followed by the Armeen T. The reaction mixture was then worked up as in Example 80 and the pigment obtained was similar to that obtained in Example 80, having the same desirable properties when dispersed in printing ink media, resulting in an ink stable to storage.

Example 82.

The same solutions and reaction conditions were used as in Example 80, but the procedure was somewhat altered in that solution (2) was coupled first with solution (1) and then suspension (3) added to the reaction mixture. The pigment compositions obtained were similar to that obtained in Example 80, and gave storage stable gravure inks.

Examples 83—85.

The procedures outlined in Examples 80—82 were repeated, replacing the Armeen T by an equal weight of Duomeen T. The pigment compositions obtained had similar excellent properties to the compositions of Examples 80—82 and gravure inks prepared from them were storage-stable.

Example 86—88.

The procedures described in Examples 80—82 were repeated, using however the equivalent quantity of 4:4'-diamino-2:2'-biphenyl disulphonic acid in place of 4:4'-diamino-5:5'-dimethyl-2:2'-biphenyl disulphonic acid. The pigment compositions obtained were stronger and more transparent than the pigment obtained simply by coupling 3:3'-dichlorobenzidine and acetoacetanilide, with similar advantages to the products obtained in Examples 80—82, and roto-gravure inks prepared from them were storage stable.

Examples 89—91.

The procedure described in Examples 86—88 were repeated, replacing the Armeen T by an equal weight of Duomeen T. The pigment compositions obtained had similar excellent properties to the pigment compositions obtained in Examples 86—88, and in addition rotogravure inks prepared from them were storage stable.

Examples 92—94.

Pigment Yellow 12, Colour Index No. 21090, was treated with 5% based on the pigment weight of the water-soluble azo dyestuff of the formula I previously defined and specific substituents as in the following Table 7, and 5% of amine on the pigment weight. The pigment was treated with combinations of any one of the water-soluble azo dyestuffs listed in Examples 92 to 94 with any one of the amines listed in Table 7.

TABLE 7

Example	X	Y	Z	n	Amines Used
92	H	SO ₃ Na	H	1	<div style="display: flex; align-items: center;"> <div style="font-size: 2em; margin-right: 5px;">{</div> <div> Armeen L15 Duomeen L15 Armeen T Duomeen T </div> </div>
93	Cl	H	4-SO ₃ Na	1	
94	H	SO ₃ Na	4-SO ₃ Na	1	

In each case excellent pigment compositions were obtained which were storage stable in gravure inks.

Examples 95—97.

The procedures described in Examples 80—82 were repeated, using however 72.5 parts of acetoacet-*o*-toluidide in place of the 67 parts of acetoacetanilide. The pigment compositions obtained were superior to that obtained simply by coupling 3:3'-dichlorobenzidine and acetoacet-*o*-toluidide, and gravure inks prepared from them were storage stable, and had similar good properties to the pigment compositions obtained in Examples 80—82.

Examples 98 and 99.

Pigment Yellow 14, Colour Index 21095, was treated with water-soluble azo dyestuff and amine as in the following Table 8. The water-soluble azo dyestuff has the formula I previously defined and was used in the proportion of 5% by weight based on the pigment dry weight. The pigment was treated with combinations of any one of the water-soluble azo dyestuffs in Examples 98 and 99 with any one of the amines listed in the last column in Table 8.

TABLE 8

Example	X	Y	Z	n	Amines used
98	H	SO ₃ Na	H	1	<div style="display: flex; align-items: center;"> <div style="font-size: 2em; margin-right: 5px;">{</div> <div> Armeen T Duomeen T </div> </div>
99	H	SO ₃ Na	4-SO ₃ Na	1	

In each case excellent pigment compositions were obtained which were storage stable in gravure inks.

Example 100.

The pigment composition described in Example 47 was treated at any of the four stages of its preparation with 15% based on the pigment weight of Armeen T, or Duomeen T. Excellent pigment compositions were obtained which were storage stable in gravure inks.

Examples 101—105.

Pigment Yellow 12, Colour Index 21090, was treated with a variety of water-soluble azo dyestuffs and a number of amines or amine oxides, the proportion of amine or amine oxide being in each case 5% based on the pigment weight with the production

of a pigment composition very suitable for use in letterpress applications. The water-soluble azo dyestuff has the formula I previously defined, specific substituents being listed in the following Table 9. The pigment was treated with combinations of any one of the water-soluble azo dyestuffs stated in Examples 101 to 105 with any one of the amines listed in the last column in Table 9.

TABLE 9

Example	X	Y	Z	n	Amines used
101	H	SO ₃ Na	H	1	Armeen T (primary amine) Duomeen T (N-long chain alkyl alkylene diamine)
102	Cl	H	4-SO ₃ Na	1	Armeen 2HT (secondary -amine) Armeen DMCD (tertiary amine)
103	CH ₃	SO ₃ Na	4-SO ₃ Na	1	Merginamide L275 (polyamide/polyamine) Rosin Amine D (resin amine)
104	H	SO ₃ Na	4-SO ₃ Na	1	Duomeen L15 (β-amine) Armeen T/Aromox C/12W (primary amine/amine N-oxide)
105	H	SO ₃ Ca $\frac{1}{2}$	H	1	Ethomeen T12 (ethox- ylated amine) Casamine C (1-amine ethyl 2-alkylimidaz- oline)(cyclic) N-(3-aminopropyl cyclohexylamine) (cyclic)

In each case, the compositions produced show enhanced flow properties, dispersibility and texture when incorporated into letterpress varnish media. The rheological properties of the inks can be controlled to some extent by the type of amine used; Rosin Amine D, Duomeen T and Armeen T treatments yield good flowing products and some increase in opacity. Merginamide L275, however, almost maintains the transparency of simple water-soluble azo dyestuff treatments and gives only a slight improvement in flow properties. Best results are obtained in application properties when the water-soluble azo dyestuffs are added before the coupling stage and amine treatment is after the coupling or boiling stages.

Example 106.

(1) A tetrazo solution was made from 26.00 parts 3:3'-dichlorobenzidine in 500 parts water.

(2) A tetrazo suspension was made from 2.00 parts 4:4'-diamino-2:2'-biphenyl disulphonic acid in 120 parts water.

46.85 parts of acetoacet-meta-xylylidide were dissolved in a solution of 900 parts water containing 9.15 parts of sodium hydroxide. The acetoacet-*m*-xylylidide was then precipitated by adding a solution of 13.75 parts of glacial acetic acid in 50 parts of water, with the formation of a slurry.

Tetrazo solution (1) was then added over 1½ hours to the slurry of precipitated acetoacet-*m*-xylylidide. The pH of the reaction mixture was maintained between 4.0 and 4.5 during the addition by the simultaneous addition of a 10% aqueous solution of sodium hydroxide.

The pH of the yellow pigment slurry obtained was then adjusted to pH 6.0 with 10% sodium hydroxide. Tetrazo suspension (2) was then added over 15 minutes to the

slurry. The pH of the slurry was maintained between 5.5 and 6.0 during the addition by the simultaneous addition of a 10% aqueous solution of sodium hydroxide.

A solution of 3.5 parts Armeen T in 250 parts of water containing 2.1 g. of glacial acetic acid was then added to the pigment slurry. The slurry was boiled for 1 hour and the pH was adjusted with 10% caustic soda solution to 8.0—9.0. The pigment composition was then isolated by filtering, washing the filter cake free of water-soluble impurities, and drying at 50° C.

The pigment obtained in this way was compared with the pigment obtained simply by coupling the pigment benzidine and coupling component without any sulphonated benzidine and with no subsequent amine treatment, and with the pigment obtained by coupling in the presence of the sulphonated benzidine but with no subsequent amine treatment. At 28.6% weight/weight in a standard letterpress printing ink medium, the pigment according to the invention gave an ink with the best rheological properties, tinctorial strength, transparency and gloss.

Examples 107—109.

The procedure described in Example 106 was repeated except that the Armeen T was replaced by 3.5 parts of Duomeen T, or by 3.5 parts of Merginamide L275 or by 3.5 parts of Rosin Amine D. Similar results were obtained.

Examples 110—112.

Pigment Yellow 13, Colour Index No. 21100, was treated with a variety of water-soluble azo dyestuffs and a number of amines or amine oxides, the proportion of amine or amine oxide being in each case 5% based on the pigment weight with the production of a pigment composition very suitable for use in letterpress applications. The water-soluble azo dyestuff has the formula I previously defined, specific substituents being listed in the following Table 10 and was used in the proportion of 5% by weight based on the pigment dry weight. The pigment was treated with combinations of any one of the water-soluble azo dyestuffs listed in Examples 110 to 112 with any one of the amines listed in the last column in Table 10.

TABLE 10

Example	X	Y	Z	n	Amines used
110	H	SO ₃ Na	2,4(CH ₃) ₂	2	Armeen T (primary amine) Duomeen T (N-long chain alkyl alkylene diamine) Armeen 2HT (secondary amine) Armeen DMCD (tertiary amine) Merginamide L275 (polyamide/polyamine) Rosin Amine D (resin amine)
111	CH ₃	SO ₃ Na	2,4(CH ₃) ₂	2	Duomeen L15 (β-amine) Armeen T/Aromox C/12W (primary amine/amine N-oxide) Ethomeen T12 (ethoxylated amine) Casamine C (1-amine ethyl 2-alkylimidazoline) (cyclic) N-(3-aminopropyl cyclohexylamine) (cyclic) methylamine cyclohexylamine
112	H	SO ₃ Na	H	1	

In each case, the compositions produced show enhanced flow properties dispersibility and texture when incorporated into letter press varnish media.

Examples 113—118.

5 Pigment Yellow 14, Colour Index No. 21095, was treated with a variety of water-soluble azo dyestuffs and a number of amines, the proportion of amine being in each case 5% based on the pigment weight with the production of a pigment composition very suitable for use in letter press applications. The water-soluble azo dyestuff has the formula I previously defined, specific substituents being listed in the following Table 11 and was used in the proportion of 5% by weight based on the pigment dry weight. The pigment was treated with combinations of any one of the water-soluble azo dyestuffs listed in Examples 113 to 118 with any one of the amines listed in Table 11.

TABLE 11

Example	X	Y	Z	n	Amines used
113	Cl	H	4-SO ₃ Na	1	<div style="display: flex; align-items: center;"> <div style="font-size: 2em; margin-right: 5px;">{</div> <div>Armeen T</div> </div> <div style="display: flex; align-items: center;"> <div style="font-size: 2em; margin-right: 5px;">{</div> <div>Duomeen T</div> </div> <div style="display: flex; align-items: center;"> <div style="font-size: 2em; margin-right: 5px;">{</div> <div>Rosin Amine D</div> </div>
114	H	SO ₃ Na	H	1	
115	CH ₃	SO ₃ Na	H	1	
116	H	SO ₃ Na	2-CH ₃	1	
117	CH ₃	SO ₃ Na	2-CH ₃	1	
118	H	SO ₃ Na	4-SO ₃ Na	1	

15 The compositions obtained show improvement in transparency gloss and tinctorial strength when incorporated in letterpress varnish media.

Examples 119—121.

The procedure used in Examples 45, 47 and 48 was repeated except that 5% based on the pigment weight of

- 20 (a) Armeen T
(b) Duomeen T
or (c) Rosin amine D

were added before the pigment suspension was boiled and filtered. Pigment compositions were obtained which showed excellent properties when incorporated into letterpress varnish media.

Examples 122—124.

25 Pigment Orange 15, Colour Index 21130, was treated with a variety of water-soluble azo dyestuffs and a number of amines, the proportion of dyestuff and amine being in each case 5% based on the pigment weight with the production of a pigment composition very suitable for use in letterpress applications. The water-soluble azo dyestuff has the formula II previously defined, specific substituents being listed in the following Table 12. The pigment was treated with combinations of any one of the water-soluble azo dyestuffs listed in Examples 122 to 124 with any one of the amines listed in Table 12.

TABLE 12

Example	X	Y	Z	n	Amine used
122	H	SO ₃ Na	H	1	{ Armeen T Duomeen T Rosin Amine D
123	H	SO ₃ Na	4-SO ₃ Na	1	
124	Cl	H	4-SO ₃ Na	1	

Products with outstanding tinctorial strength, transparency and gloss are obtained.

Example 125.

5 Solution (1) Tetrazo 3,3'-dichlorobenzidine was prepared by tetrazotising 77.10 parts 3,3'-dichlorobenzidine in 1500 parts of water at 0° C.

Suspension (2) Tetrazo 4,4'-diamino-2:2'-biphenyl disulphonic acid was prepared by tetrazotising 5.35 parts 4,4'-diamino-2:2'-biphenyl disulphonic acid in water at 0° C.

10 Solution (3) 126 parts 1-p-tolyl-3-methyl-5-pyrazolone were dissolved in a solution of 37.8 parts sodium hydroxide in 900 parts water.

A solution of 7.2 parts sodium acetate in 2000 parts water was prepared in a coupling vessel. The pH was adjusted to 5.0 with dilute hydrochloric acid and solutions (1) and (3) run in simultaneously at ambient temperature over the course of 30 minutes ensuring that at no time was any substantial quantity of uncoupled tetrazo present. Suspension (2) was then added over 10 minutes to the reaction mixture from solutions (1) and (3).

20 5 parts of Armeen T dissolved in dilute acetic acid was then added to the reaction mixture. The resultant reaction mixture was heated to 90° C and held at 90° C for 30 minutes. The pigment was then filtered off, washed with water and dried at 50—55°C.

When incorporated into a letterpress varnish medium, the pigment thus prepared had better tinctorial strength than an untreated pigment, together with good rheological properties and adequate texture.

Examples 126 and 127.

25 Pigment Orange 34, Colour Index No. 21115 was treated with a variety of water-soluble azo dyestuffs and a number of amines, the proportion of amine being in each case 5% based on the pigment weight with the production of a pigment composition very suitable for use in letterpress applications. The water-soluble azo dyestuff has the formula II as previously defined, specific substituents being listed in the following Table 13. The pigment was treated with combinations of any one of the water-soluble azo dyestuffs listed in Examples 126 and 127 with any one of the amines listed in Table 13.

TABLE 13

Example	X	Y	Z	n	Amine used
126	H	SO ₃ Na	H	1	{ Armeen T Duomeen T
127	Cl	H	4-SO ₃ Na	1	
					{ Rosin Amine D

Products with outstanding tinctorial strength, transparency and gloss are obtained.

Examples 128—130.

The procedures described in Examples 65, 66 and 68 were repeated except that 5% on pigment weight of

- 5 (a) Duomeen T
or (b) Rosin amine D

5

were incorporated before the pigment suspension was boiled and filtered. The products showed advantages of flow and texture/dispersibility in letterpress varnish media.

An example will now be given of the incorporation of resin into a pigment composition according to the invention:—

10

Example 131.

10

The procedure described in Example 16 was repeated except that 25% by weight (calculated on the weight of the pigment) of a magnesium salt of wood rosin was added to the coupling vessel before the coupling was started.

15

The pigment composition was compared with the equivalent resinated pigment which had not been treated with the water-soluble azo dyestuff. In letterpress inks the dyestuff treated pigment produced a more transparent, tinctorially stronger print than did the other.

15

An example will now be given of the solvent treatment and incorporation of amine into a pigment:—

20

Example 132.

20

The procedure described in Example 70 was repeated as far as the preparation of the pigment/dyestuff slurry. To the slurry was then added 5 parts by weight of cetyl alcohol in place of the dibenzyl ether. The slurry was boiled for 1 hour, cooled to 70° C. with cold water, and 6 parts by weight of each of Rosin Amine D and acetic acid in water were added. The pH of the slurry was raised to pH 9—10 with 10% caustic soda solution. The slurry was then filtered, washed and dried at 50° C.

25

25

This product possessed greater tinctorial strength, gloss and transparency in letterpress ink media than did untreated pigment.

Two Examples will now be given of the water-soluble azo dyestuff treatment of mixed couplings:—

30

30

Example 133.

Tetrazo 3,3'-dichlorobenzidine was made in the usual way from 54.8 parts of 100% 3,3'-dichlorobenzidine.

35

47.0 parts of acetoacet-meta-xylylide and 40.6 parts of acetoacetanilide were dissolved in 27 parts of sodium hydroxide in 1300 parts of water.

35

In a coupling vessel were dissolved 50 parts of sodium acetate in 500 parts of water. 10% of the coupling component solution was added and the pH of the solution adjusted to below 7.0 with dilute hydrochloric acid.

40

Both coupling component and tetrazo solutions were then run in simultaneously at equal rates over 1 hour at room temperature.

40

After coupling the slurry was split into four equal parts.

A. This part was boiled for 1 hour, filtered and the pigment washed and dried at 50° C.

45

B. To the second part was added 5% based on the pigment weight of the water-soluble azo dyestuff prepared from coupling tetrazo benzidine-2,2'-disulphonic acid with an equal molar mixture of acetoacetanilide and acetoacetmeta-xylylide. The water-soluble azo dyestuff had previously been dissolved in hot water.

45

The slurry was then boiled for 1 hour, filtered, and the pigment washed and dried at 50° C.

50

C. To the third part, 5% based on the pigment weight of the dyestuff used in (B) was added (dissolved in hot water) and the slurry stirred for 5 minutes. 5% based on the pigment weight of Rosin Amine D dissolved in dilute hot acetic acid was added. The slurry was then boiled for 1 hour, filtered, and the pigment washed and dried at 50° C.

50

55

D. To the fourth part, 5% based on the pigment weight of the dyestuff used in (B) was added (dissolved in hot water), 5% based on the pigment weight of cetyl alcohol was added and the slurry was boiled 1 hour, filtered, and the pigment washed and dried at 50° C.

55

60

B, C and D showed strength and transparency advantages over the control A in letterpress ink media, B in addition showing gloss advantages. C and D both had better flow and dispersibility properties than B.

60

Example 134.

Tetrazo 3,3'-dichlorobenzidine was prepared by tetrazotising 25.3 parts of 3,3'-dichlorobenzidine.

5 This was coupled by a simultaneous process to a mixture of 17.4 parts of 1-phenyl-3-methyl-5-pyrazolone and 18.8 parts of 1-*p*-tolyl-3-methyl-5-pyrazolone at pH 4.5—5.0 at room temperature. An aqueous solution of 5% based on the pigment weight of a water-soluble azo dyestuff prepared from coupling tetrazo benzidine-2:2'-sulphonic acid with an equimolar mixture of 1-phenyl-3-methyl-5-pyrazolone and 1-*p*-tolyl-3-methyl-5-pyrazolone was added to the pigment slurry. The slurry was then heated to 90° C and held at that temperature for 30 minutes. It was then filtered, washed and dried at 50° C.

10 When the properties of this pigment composition are compared with a pigment composition which had not been treated with water-soluble azo dyestuff during its preparation, it is found that in letterpress varnish transparency and gloss advantages are present.

15 If both water-soluble azo dyestuff and amine treatments are employed in the mixed coupling process, then flow and dispersibility advantages are found over the simple water-soluble azo dyestuff treatments.

20 WHAT WE CLAIM IS:—

1. A process in which a diarylide pigment composition is produced which comprises coupling in water a tetrazotised pigment benzidine (as hereinbefore defined) with a pigment coupling component (as hereinbefore defined) and incorporating in the pigment whilst still in the water a water-soluble azo dyestuff.

25 2. A process in which a diarylide pigment composition is produced which comprises coupling in water a tetrazotised pigment benzidine (as hereinbefore defined) with a pigment coupling component (as hereinbefore defined) and incorporating in the pigment whilst still in the water a water-soluble disazo diarylide dyestuff.

30 3. A process according to claim 2 in which there is used in the coupling a stoichiometric excess of the pigment coupling component over the tetrazotised pigment benzidine and a minor proportion of a tetrazotised sulphonated benzidine or tetrazotised carboxylated benzidine is added to the tetrazotised pigment benzidine before the coupling, or to a portion of the pigment coupling component before the coupling or to the reaction mixture during or after the coupling.

35 4. A process according to claim 2 in which a water-soluble disazo diarylide dyestuff is added to the tetrazotised pigment benzidine before the coupling or to a portion of the pigment coupling component before the coupling or to the reaction mixture during or after the coupling.

40 5. A process according to claim 2 in which a water-soluble disazo diarylide dyestuff is added to a previously prepared diarylide pigment.

6. A process according to claim 2 in which the coupling of the pigment is conducted in a solution of a water-soluble disazo diarylide dyestuff.

45 7. A modification of a process according to any one of claims 2—6 in which the water-soluble disazo diarylide dyestuff is rendered insoluble *in situ* in the composition.

8. A process according to claim 2 in which a resin or resinous material is incorporated into the composition.

9. A process according to claim 2 in which a surface-active agent is incorporated into the composition.

50 10. A process according to claim 1 substantially as described in Example 29 herein.

11. A process according to claim 2 substantially as described in any one of Examples 1—3, 16—28, 30—32 and 35—37 herein.

12. A process according to claim 1 substantially as described in any one of Examples 4—15, 33, 34 and 38—68 herein.

55 13. A process according to claim 8 substantially as described in Example 131 herein.

14. A diarylide pigment composition comprising a diarylide pigment and an insoluble metal salt of an otherwise water-soluble azo dyestuff.

60 15. A diarylide pigment composition comprising a diarylide pigment and either a water-soluble disazo diarylide dyestuff or an insoluble metal salt of an otherwise water-soluble disazo diarylide dyestuff.

16. A composition according to claim 14 or claim 15 in which the diarylide pigment is a benzidine yellow or a benzidine orange.

17. A composition according to any of claims 14 to 16 containing from 1 to 10% by weight of water-soluble azo dyestuff calculated on the pigment.

18. A diarylide pigment composition prepared by a process according to claim 1 or claim 10.

19. A diarylide pigment composition prepared by a process according to any one of claims 2 to 7 and 11.

20. A diarylide pigment composition prepared by a process according to any one of claims 8, 9 and 12.

21. A diarylide pigment composition prepared by a process according to claim 13.

22. A process according to claim 2 in which the pigment composition in the aqueous state, is subjected to a conventional solvent treatment or has incorporated in it a fatty alcohol, diol or polyol containing from 8 to 22 carbon atoms.

23. A process according to claim 22 in which an aqueous paste or aqueous suspension of the pigment composition is boiled with tetralin, dibenzyl ether or *o*-dichlorobenzene, and the pigment composition then filtered off.

24. A process according to claim 22 in which 0.1 to 30% by weight based on the weight of the dry pigment of a fatty alcohol, diol or polyol containing from 8 to 22 carbon atoms is added to the pigment coupling component before the coupling, or to the pigment benzidine before or after diazotisation and before the coupling, or to the reaction mixture during or after the coupling.

25. A process according to claim 22 in which the diarylide pigment composition is formed into an aqueous slurry, 0.1 to 30% by weight based on the weight of the dry pigment of a fatty alcohol, diol or polyol containing from 8 to 22 carbon atoms is added to the slurry with agitation and heating, and the pigment composition subsequently filtered off, washed and dried.

26. A process according to claim 24 or claim 25 in which from 0.1 to 10% by weight of the alcohol, diol or polyol is used calculated on the dry pigment composition being prepared or treated.

27. A process according to any one of claims 23, 25 and 26 in which the alcohol, diol or polyol is present during the coupling or is added to the reaction mixture during the coupling and a non-ionic surface active agent is also present during the coupling.

28. A process according to any one of Claims 22 to 27 in which a metallic salt of a resin or the free resin itself is added to the pigment composition.

29. A process according to claim 2 in which a fatty acid or fatty ester is incorporated in the pigment composition.

30. A process according to claim 22 substantially as described in any one of Examples 70, 71, 74 and 78 herein.

31. A process according to claim 22 substantially as described in any one of Examples 69, 72, 73, 75—77 and 79 herein.

32. A process according to claim 26 substantially as described in either Example 69 or 72 herein.

33. A diarylide pigment composition comprising a diarylide pigment and either a water-soluble azo dyestuff or an insoluble metal salt of an otherwise water-soluble azo dyestuff together with a fatty alcohol, diol or polyol containing from 8 to 22 carbon atoms.

34. A diarylide pigment composition as claimed in Claim 33 in which the azo dyestuff is a disazo diarylide dyestuff.

35. A diarylide pigment composition prepared by a process according to any one of claims 22—30.

36. A diarylide pigment composition prepared by a process according to claim 31.

37. A process according to claim 2 in which there is incorporated in the pigment composition 0.1 to 35% calculated on the weight of the pigment and dyestuff of an aliphatic amine, amine salt or amine oxide containing from 1 to 20 carbon atoms.

38. A process according to claim 37 in which a salt of an amine containing from 1 to 20 carbon atoms is added to an acidic aqueous slurry of the pigment composition, the pH is then raised to alkaline and the slurry is then boiled.

39. A process according to claim 37 in which an acidic aqueous slurry of the pigment composition is boiled, a salt of an amine containing from 1 to 20 carbon atoms is then added, and the pH is then raised to alkaline.

40. A process according to claim 37 in which a salt of an amine containing from 1 to 20 carbon atoms is added to an acidic aqueous slurry of the pigment composition, the slurry is then boiled, and the pH is raised to alkaline.

41. A process according to claim 37 in which an acidic aqueous slurry of the

pigment composition is made alkaline, a salt of an amine containing from 1 to 20 carbon atoms is then added and the slurry is then boiled.

42. A process according to claim 37 in which an acidic aqueous slurry of the pigment composition is made alkaline, the slurry is then boiled and then a salt of an amine containing from 1 to 20 carbon atoms is added.

43. A process according to claim 37 in which an acidic aqueous slurry of the pigment composition is boiled, the slurry is then made alkaline and then a salt of an amine containing from 1 to 20 carbon atoms is added.

44. A process according to claim 37 in which a salt of an amine containing from 1 to 20 carbon atoms is added to an acidic aqueous slurry of the pigment composition, and the slurry is then boiled.

45. A process according to claim 37 in which an acidic aqueous slurry of the pigment composition is boiled, and then a salt of an amine containing from 1 to 20 carbon atoms is added.

46. A process according to claim 37 in which the amine or amine oxide is present during the coupling, or is added to the tetrazotised pigment benzidine or to the pigment coupling component before the coupling.

47. A process according to claim 37 substantially as described in any one of Examples 80—91, 95—97, 106—109 and 125 herein.

48. A process according to claim 37 substantially as described in any one of Examples 92—94, 98—105, 110—124 and 126—130 herein.

49. A diarylide pigment composition comprising a diarylide pigment and either a water-soluble azo dyestuff or an insoluble metal salt of an otherwise water soluble azo dyestuff together with an aliphatic amine, amine salt or amine oxide containing from 1 to 20 carbon atoms.

50. A diarylide pigment composition as claimed in claim 49 in which the azo dyestuff is a disazo diarylide dyestuff.

51. A diarylide pigment composition according to claim 49 or claim 50 which contains one or more of free amine, amine salt, amine salt of the water-soluble azo dyestuff, azomethine compound of the water-soluble azo dyestuff and amine salt of the azomethine compound of the water-soluble azo dyestuff.

52. A diarylide pigment composition according to claim 49 or claim 50 containing from 0.1 to 10% by weight calculated on the composition of the amine, amine salt or amine oxide.

53. A diarylide pigment composition according to claim 49 or claim 50 containing more than 10% by weight calculated on the composition of the amine, amine salt or amine oxide.

54. A diarylide pigment composition prepared by a process according to any one of claims 37—47.

55. A diarylide pigment composition prepared by a process according to claim 48.

56. A process according to claim 22 and claim 37 in which the pigment composition, in the aqueous state, is subjected to a conventional solvent treatment and has incorporated in it 0.1 to 35% calculated on the weight of the pigment and dyestuff of an aliphatic amine, amine salt or amine oxide containing from 1 to 20 carbon atoms.

57. A process according to claim 56 substantially as described in Example 132 herein.

58. A diarylide pigment composition prepared by a process according to claim 56 or claim 57.

59. A process according to claim 2, claim 22 or claim 37 substantially as described in Example 133 herein.

60. A process according to claim 2, substantially as described in Example 134 herein.

61. A diarylide pigment composition prepared by a process according to claim 59 or claim 60.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, L1 3AB,
Chartered Patent Agents.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.